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Butadiene polymerisation process.

Catalytic polymerisation of butadiene to cis-1,4-polybutadiene, conducted in the absence or substantial absence of solvents or diluents.

According to said process, a catalytic mixture is prepared by bringing into contact, in a hydrocarbon vehicle, one or more neodymium compounds, one or more halogen contributor compounds, one or more compounds containing hydroxyls, and an aluminium organometal and/or hydride compound.

Said catalytic mixture is brought into contact with liquid butadiene monomer, and the resultant mixture is fed continuously to one end of an elongated plug-flow polymerisation reactor in which the butadiene is polymerised.

Alternatively, said polymerisation reactor is fed continuously with a stream of the catalytic mixture and a stream of liquid butadiene. The heat of polymerisation is removed by partial evaporation of the butadiene monomer, so that by controlling the pressure of this latter it is possible to maintain the polymerisation temperature within the predetermined range. By also controlling the catalyst composition, the butadiene monomer/catalyst ratio, the polymerisation temperature and the residence time in the reactor, it is possible to produce mixtures containing from about 25% to about 70% of polymer by weight, which are discharged continuously from the other end of the polymerisation reactor.

The cis-1,4-polybutadiene is recovered as final product from the discharged mixture by evaporating the unreacted butadiene and any solvent used as the catalyst vehicle from the polymer mass, to which a short stopper for the catalyst and stabilisers against thermo-oxidative degradation have been added.

This evaporation takes place in an extruder-desolventiser.

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This invention relates to the production of cis-1,4-polybutadiene by catalytic polymerisation of butadiene monomer by means of a continuous process conducted in the absence or substantial absence of solvents or diluents.

Various catalytic processes for butadiene polymerisation are known in the art which are able to produce polybutadiene with a high content of cis-1,4 units, this being particularly suitable for the manufacture of tyres and other elastomer articles. The catalysts generally used for this purpose derive from a combination of compounds of transition metals such as titanium, cobalt, nickel, uranium and rare earth metals, with alkyl and/or hydride derivatives of metals of Groups IA, IIA and IIIA of the periodic system, such as described in USA patents 3,118,864, 3,178,402, 3,794,604 and 4,242,232, and in Belgian patents 559,676, 573,680 and 791,709.

In processes of the known art, butadiene polymerisation is mostly conducted in a hydrocarbon solution in order to control the polymerisation temperature and thus obtain soluble linear polymers free or substantially free from gel, and having a controlled molecular weight.

The production of cis-1,4-polybutadiene by bulk polymerisation has however not found significant development in industrial practice, in spite of the undoubted advantages which a process conducted in the absence or substantial absence of solvents or diluents has over a conventional process in solution.

The reasons for this lack of success are mainly as follows:

A) the lack of identification of suitable catalytic systems which possess the combination of characteristics required by bulk polymeri-

sation, and more particularly:

- that they should not give rise, in the presence of an excess of monomer, to transfer reactions responsible for producing low molecular weight polymers of little use in applications;
- 5 - that they should not give rise to secondary cross-linking, cyclisation and/or branch reactions in the polymer which are responsible for the formation of considerable quantities of gel, which has a strongly negative effect on the required characteristics of the final product;
- 10 - that they should have sufficiently high activity so that the final polymer contains a low level of catalytic residues, so as to dispense with the need for washing;
- that they should maintain high activity and selectivity under high temperature conditions such as those required for operating
- 15 in a highly viscous system with sufficient reaction kinetics;

B) The engineering, rheological and heat transfer difficulties connected with the processing of highly viscous masses.

The object of the present invention is therefore a process which, by the combination of a suitable catalytic system and an adequate

- 20 fluorodynamic system enables the aforesaid difficulties to be overcome in order to obtain high molecular-weight linear cis-1,4-polybutadiene at high yield and free from gel, by polymerisation conducted in the absence of low-boiling hydrocarbon solvents or diluents, or in the presence of a minimum quantity of said low-boiling solvents or diluents
- 25 generally equal to or less than about 2% by weight with respect to the butadiene monomer.

More particularly, according to the present invention:

- a catalytic mixture is prepared by bringing into contact, in an inert hydrocarbon vehicle:

- a) at least one neodymium compound chosen from neodymium oxide, alcoholates, phenates and carboxylates;
- 5 b) at least one organic compound containing hydroxyl (alcoholic or phenolic) or carboxyl groups chosen from alcohols, phenols and carboxylic acids, with the possible addition of water;
- c) at least one halogenated compound chosen from secondary or tertiary alkyl halides, aryl or alkylaryl halides, organic
10 acid halides, metal or organometal halides, hydrogen halide acids and halogens;
- d) at least one aluminium organometal compound or relative hydride derivatives;

the quantities of compounds a) and b) being such that the ratio of
15 hydroxyl and/or carboxyl groups to the neodymium atoms is between 2:1 and 100:1; and keeping said components in contact in order to obtain a catalytic mixture in which the aluminium:neodymium atomic ratio is between 20:1 and 200:1, and the halogen:neodymium atomic ratio is between 0.2:1 and 3:1;

- 20 - continuously feeding said catalytic mixture and liquid butadiene monomer, possibly mixed together, in the proportion of between 4.10^4 and 4.10^5 g.moles of butadiene per g.atom of neodymium, to one end of an elongated polymerisation reactor in which the mixture is polymerised under plug-flow conditions, while maintaining an inlet temperature
25 of not less than 30°C and an outlet temperature of not greater than 130°C and controlling the temperature within said range by partial

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evaporation of butadiene monomer from the liquid polymerisation phase, until a mixture is obtained having a polymer content of between about 25% and about 70% by weight, this being discharged from the other end of the reactor;

- 5 - the cis-1,4-polybutadiene is separated and recovered from said discharged mixture.

The vehicle used for the catalyst according to the present invention can be constituted by low-boiling or relatively low-boiling inert (non-reactive) hydrocarbons such as butane, pentane, hexane and
10 heptane, linear or branched, or their mixtures. These hydrocarbons, introduced with the catalyst, are separated from the polybutadiene at the end of the polymerisation stage.

According to a further embodiment, the catalyst vehicle is constituted by hydrocarbons or hydrocarbon mixtures of high molecular weight
15 such as paraffin oil and the like, or hydrocarbon oils required for oil-extended polybutadiene formulations.

These hydrocarbons do not require separation and remain incorporated in the polybutadiene. In particular, it has been found that when the content of paraffin oil and the like is less than about 5% by
20 weight in the polymer, the characteristics of these latter are not appreciably modified.

The neodymium compounds used in the catalyst preparation are chosen from neodymium oxide (Nd_2O_3), neodymium alcoholates derived from aliphatic and cycloaliphatic alcohols, neodymium phenates and neodymium
25 carboxylates derived from aliphatic, cycloaliphatic and aromatic organic acids. Of these, the preferred compounds are neodymium oxide, neodymium tributylat and neodymium trinaphthenates.

The organic compounds containing hydroxyl groups (alcoholic or phenolic) or carboxyl groups are chosen from aliphatic and cycloaliphatic alcohols, phenols and substituted phenols, and aliphatic, cycloaliphatic and aromatic acids.

- 5 Of these, butyl alcohol and naphthenic acids are preferred. These compounds can be used in free form or partially or totally combined with the neodymium (neodymium alcoholates, phenates and carboxylates), provided the ratio of hydroxyl groups (including those of water) and/or combined carboxyl groups to neodymium atoms is in the range of between
10 2:1 and 100:1.

- It has been found that the addition of small quantities of water as a hydroxyl contributor is desirable in that it improves the catalyst activity. More particularly, this effect of the water is manifested on maintaining the ratio of aluminium atoms in the aluminium organometal
15 compound or relative hydride derivative to the added moles of water within a range of between 1:1 and 5:1, with a preferred value of around 2:1.

- The halogen contributor compounds used in the catalyst preparation are preferably chosen from hydrochloric acid, diethyl aluminium chloride,
20 ethyl aluminium dichloride, aluminium trichloride, tert.butyl chloride, benzyl chloride and benzoyl chloride. In particular, hydrochloric acid can be fed in the form of aqueous hydrochloric acid, so as to also provide the desired water quantity.

- The aluminium organometal compounds and relative hydride derivatives
25 are the aluminium trialkyls and aluminium alkyl hydrides. Preferably triethylaluminium, triisobutylaluminium and diisobutylaluminium monohydride are used.

The quantities of the various catalyst components are chosen so as to respect an aluminium:neodymium atomic ratio of between 20:1 and 200:1, and a halogen:neodymium atomic ratio of between 0.2:1 and 3:1.

In the preferred embodiment, the aforesaid ratios are of the order
5 of between 3:1 and 30:1 for the ratio of hydroxyl groups (including those of water) and/or carboxyl groups to neodymium atoms, of the order of between 25:1 and 80:1 for the ratio of aluminium atoms to neodymium atoms, and of the order of between 1:1 and 2:1 for the ratio of halogen atoms to neodymium atoms.

10 According to the process of the present invention, the catalytic mixture is prepared by bringing the aforesaid catalytic components into contact in the hydrocarbon vehicle, operating at a temperature equal to or greater than ambient.

The order and manner of adding the catalytic components are not
15 critical, however according to one embodiment the components are brought into contact in the hydrocarbon vehicle in the following order at ambient temperature (20°-25°C):

- neodymium alcoholate, phenate and/or carboxylate;
- aluminium organometal compound and/or relative hydride derivative;
- 20 - halogenated compound;
- hydroxyl and/or carboxyl compound and possibly water.

According to a further embodiment, they are brought into contact in the hydrocarbon vehicle in the following order at a temperature of 50°-80°C:

- 25 - neodymium oxide;
- hydroxylated and/or carboxylated organic compound;
- halogenated compound;

- water.

The mixture is then cooled to ambient temperature (20°-25°C) and an aluminium organometal compound or relative hydride derivative is added.

- 5 By operating in the aforesaid manner, a catalytic solution is obtained, or alternatively a catalytic mixture in which the catalyst is for the most part dissolved in the relative hydrocarbon vehicle.

The catalytic mixture prepared in this manner is mixed with liquid butadiene monomer in a proportion such as to obtain a ratio of g.moles
10 of butadiene to g.atoms of neodymium of between $4 \cdot 10^4$ and $4 \cdot 10^5$. The mixing can be carried out in any device which ensures good homogenisation, for example an agitated vessel. Mixing is carried out at a temperature suitably chosen to prevent rapid butadiene polymerisation before its entry into the polymerisation reactor, and preferably at
15 a temperature of between 20° and 30°C.

In a further embodiment, a stream of the catalytic mixture and a stream of liquid butadiene are independently fed into the polymerisation reactor, in quantities such as to respect the aforesaid ratios.

In all cases, the feed takes place at one end of an elongated polymeri-
20 sation reactor in which the mixture can flow under plug-flow or substantially plug-flow conditions. Extruders in which the mass under polymerisation is driven by single-screw or double-screw self-cleaning agitators are for example suitable.

The polymerisation is generally conducted between an inlet temperature
25 of not less than 30°C and an outlet temperature of not more than 130°C, and preferably between an inlet temperature of the order of 50°-60°C and an outlet temperature of the order of 80°-100°C, so as to allow

the mass to flow, the mass becoming increasingly more viscous as the polymerisation proceeds.

The temperature is controlled by partially evaporating the butadiene monomer, which can be recycled to the polymerisation stage after
5 condensation, without any need for purification.

A certain quantity of the heat of polymerisation can also be removed by feeding cold streams to the polymerisation reactor.

The pressure at which the polymerisation is conducted is such as to ensure that the butadiene monomer is present in the liquid phase.

10 For the aforesaid temperature range, said pressure is conveniently chosen between 3 and 18 bars absolute.

When operating within the aforesaid general conditions, a mixture is discharged at the other end of the reactor having a polymer content of between about 25% and about 70% by weight, when operating
15 with a residence time of between 10 and 120 minutes. Under the preferred operating conditions, the residence time is of the order of 20-60 minutes. For reasons of economy, it is convenient to operate with a relatively high conversion value for the conversion of butadiene into the relative polymer, so as to discharge mixtures
20 with a polymer content of 60-70% by weight from the reactor.

According to one embodiment of the present invention, the mixture leaving the polymerisation reactor is fed to a mixing device in which polymerisation arresting (short stopper) agents and stabilisers against polymer thermo-oxidative degradation, preferably in solution
25 in butadiene, are fed. The catalyst is deactivated by preferably using water or higher aliphatic alcohols (containing for example between 8 and 18 carbon atoms in the molecule) in such a quantity

as to exceed the sum of the catalytic components by at least 5-10 times.

Basifying agents soluble in the short stopper, such as ammonia, amines, epoxides and organic salts (alcoholates and carboxylates) of alkaline metals, are preferably added thereto.

In addition to the usual antioxidants for preserving the polymer, such as sterically hindered phenols and phosphites, radical capturing agents such as secondary amines and the said epoxides are also preferably added to the hydrocarbon solution. The two solutions can conveniently be emulsified together.

The mass treated in this manner is then fed to a further heated screw device (extruder-desolventiser), where the volatile substances are removed by evaporation, by operating at a temperature in the range of 100° to 180°C and a pressure equal or close to atmospheric pressure.

This treatment removes the unconverted butadiene, any low-boiling solvent introduced with the catalytic mixture, and any water introduced in excess to that required for the destruction of the catalytic system. The butadiene and any low-boiling solvent are subjected to the usual treatments for their separation and recycling.

By operating in accordance with the process of the present invention, a polybutadiene is typically obtained in dry stabilised form, with a volatile substance content less than about 1% by weight.

This polybutadiene also has a content of cis-1,4 units which generally exceeds 97%, and a Mooney viscosity (M.L. 1+4, 100°C) of from 30 to 80 and by nd.

Consequently with the process of the present invention, it is possible

to obtain a linear polybutadiene free from gel and with a very high content of cis-1,4 units. Said polymer requires no washing for separating the catalytic residues.

Moreover, the process of the present invention is simple and convenient, has low energy consumption, and presents no problems of an ecological character, given that there are no effluents.

The experimental examples given hereinafter are illustrative of but do not limit the present invention.

EXAMPLE 1

10 With reference to Figure 1, the vessel 10 which has a capacity of 5 l, and is provided with an agitator and a heat transfer system, is fed under a nitrogen atmosphere with the following through the line 22:

- 130 g (0.367 moles) of 95% neodymium oxide (Nd_2O_3);
- 15 - 549 g (2.255 moles) of naphthenic acid, with an acid value of 230;
- 6.1 ml of an aqueous 37% weight solution of hydrochloric acid;
- 854 g of n-hexane.

20 In this mixture, the ratio of carboxyl and hydroxyl groups, contributed by the naphthenic acid and water, to the number of neodymium atoms is 3.2:1.

The mixture is kept agitated in the vessel 10 under a nitrogen atmosphere at a temperature of 60°C for 3 hours. At the end of this time period, a turbid solution is obtained with the appearance of
25 an oil.

The solution obtained in this manner is fed through line 24 into the vessel 12, which has a capacity of 120 l and is provided with

an agitator. 43 l of a solution containing 0.914 mol s/l of aluminium diisobutylmonohydride in hexane are also fed into the vessel 12 through the line 26.

5 The mass is kept agitated under nitrogen at ambient temperature (about 20°C) for one hour.

At the end of this time, 530 ml of a solution containing 1.1 moles/l of aluminium ethyldichloride in hexane are fed into the vessel 12 through the line 26, and the mass is kept agitated for a further 0.5 hours under a nitrogen atmosphere at ambient temperature (about 10 20°C).

The catalytic solution obtained in this manner has the following concentrations, in terms of neodymium, aluminium and chlorine:

- neodymium: 0.0184 g.atoms/l
- aluminium: 0.8790 g.atoms/l
- 15 - chlorine: 0.0275 g.atoms/l.

Consequently the chlorine:neodymium atomic ratio is about 1.5:1 and the aluminium:neodymium atomic ratio is about 48:1.

The catalytic solution is withdrawn from the vessel 12 through the line 28 at a throughput of 455 ml/hour, and is mixed with anhydrous 20 liquid butadiene which is fed through the line 30 at a throughput of 36 l/hour.

Said butadiene comes partly from the fresh butadiene drying section (not shown) through the line 32 (approximately 13 l/hour) and partly by recycling from the reactor 16 through the line 34 (about 23 l/hour) 25 after condensation in 36.

The butadiene and catalytic solution are fed through the line 38 to the mixer 14, which has a capacity of 1.5 l and is fitted with

an agitator. The mixing temperature is about 30°C.

The mixture leaving the mixer 14 is fed through the line 40 to the polymerisation reactor 16. The reactor 16 is a reactor of the self-cleaning screw type, with a total volume of 23 l and a useful
5 volume of 16 l, in which the mixture being polymerised flows with plug-flow. The reactor 16 is operated under a pressure of 6.7 bars with an inlet temperature of about 60°C and an outlet temperature of about 90°C. The heat of polymerisation is removed by partial evaporation of the butadiene, which is withdrawn through the line
10 34 and recycled after condensing in the condenser 36.

Under these conditions, a mixture containing about 70% by weight of polymer is discharged from the reactor 16 and is fed to the screw device 18, into which a solution containing 100 g/l of a commercial antioxidant in butadiene is fed at a throughput of 300 ml/hour through
15 the line 42. Water is fed at a throughput of 150 ml/hour to a point further downstream in the device 18, through the line 44.

The mass treated in this manner is fed to the device 20 for elimination of the volatile components, and in which the residual butadiene, hexane and water are removed at a temperature of 130°C at atmospheric
20 pressure, and are fed to the separation section (not shown) through the line 46.

6 kg/hour of anhydrous butadiene polymer are recovered from the device 20 through the line 48, and has the following characteristics:

- Mooney viscosity (M.L., 1+4, 100°C): 40
- 25 - content of cis-1,4 units: 98% (infrared determination)
- ratio of the weighted average molecular weight to the numerical average molecular weight (Mw:Mn): 6.2 (determination by gel

permeation chromatography)

- content of volatile substances: 0.5% by weight.

EXAMPLE 2

With reference to Figure 1, the vessel 10, which has a capacity of 5 l and is provided with an agitator and a heat transfer system, is fed under a nitrogen atmosphere with the following through the line 22:

- 129 g (0.364 moles) of 95% neodymium oxide (Nd_2O_3);
- 496 ml (2.037 moles) of naphthenic acid with an acid value of 230;
- 1.5 l of liquid paraffin of "vaseline oil" type.

The mixture is heated to 80°C under agitation for 2 hours, when 6 ml of an aqueous 37 weight % hydrochloric acid solution is added. After keeping the mixture at 80°C for a further two hours, it is cooled and diluted under agitation with 3 l of the aforesaid liquid paraffin.

The contents of the vessel 10 are transferred through the line 24 to the vessel 12, into which 1.15 l of a 1 molar solution of tert.butylchloride in the aforesaid liquid paraffin had been previously fed through the line 26.

The mixture is left under agitation for a further two hours at ambient temperature.

The catalytic mixture obtained in this manner has the following concentrations of neomydium, aluminium and chlorine:

- neomydium: 0.0139 g.atoms/l
- aluminium: 0.7404 g.at ms/l
- chl rine: 0.0197 g.atoms/l

Consequently the chlorine:neomydimum at mic rati is about 1.4:1
and the aluminium:neomydimum ratio about 53:1.

Proceeding in the same manner as Example 1, 438 ml/hour of the
catalytic mixture and 18 l/hour of liquid butadiene containing 80 ppm
5 of water are fed into the mixer 14. The polymerisation reactor 16
is operated with an inlet temperature of 55°C and an outlet temperature
of 84°C at a pressure of 6 bars. The screw device 18 is fed with
a hexane solution containing 50 g/l of a commercial antioxidant at
a throughput of 300 ml/hour, and also, in a parallel feed, with
10 400 ml/hour of n-decanol.

The screw device 20 is operated in the same manner as Example 1, to
discharge through the line 48 3.1 kg/hour of polybutadiene having
a content of cis-1,4 units of 97.8% and a Mooney viscosity (M.L.,
1+4, 100°C) of 45.

CLAIMS:

1. A process for preparing cis-1,4-polybutadiene by catalytic polymerisation of butadiene monomer in the absence or substantial absence of solvents or diluents, characterised in that:

5 - a catalytic mixture is prepared by bringing into contact, in an inert hydrocarbon vehicle:

- a) at least one neodymium compound chosen from neodymium oxide, alcoholates, phenates and carboxylates;
- 10 b) at least one organic compound containing hydroxyl (alcoholic or phenolic) or carboxyl groups chosen from alcohols, phenols and carboxylic acids, with the possible addition of water;
- c) at least one halogenated compound chosen from secondary or tertiary alkyl halides, aryl or alkylaryl halides, organic acid halides, metal or organometal halides, hydrogen halide
15 acids and halogens;
- d) at least one aluminium organometal compound or relative hydride derivatives;

the quantities of the compounds a) and b) being such that the ratio of hydroxyl groups (including those of water) and/or carboxyl groups
20 to the neodymium atoms is between 2:1 and 100:1;

and keeping said components in contact in order to obtain a catalytic mixture in which the aluminium:neodymium atomic ratio is between 20:1 and 200:1, and the halogen:neodymium atomic ratio is between 0.2:1 and 3:1;

25 - continuously feeding said catalytic mixture and liquid butadiene monomer, possibly premixed, in the proportion of between 4.10^4 and 4.10^5 g.m les of butadiene per g.at m f n odymium, to one end

of an elongated polymerisation reactor in which the mixture is polymerised under plug-flow conditions, while maintaining an inlet temperature of not less than 30°C and an outlet temperature of not greater than 130°C and controlling the temperature within said range by partial evaporation of butadiene monomer from the liquid polymerisation phase, until a mixture is obtained having a polymer content of between about 25% and about 70% by weight, this being discharged from the other end of the reactor;

5 - the cis-1,4-polybutadiene is separated and recovered from said discharged mixture.

2. A process as claimed in claim 1, characterised in that the hydrocarbon vehicle for the catalyst is chosen from butane, pentane, hexane and heptane, linear or branched, or their mixtures, paraffin oil or hydrocarbon oils for oil-extended polybutadiene formulations.

15 3. A process as claimed in claim 1, characterised in that the neodymium compounds are chosen from neodymium oxide (Nd_2O_3), neodymium tributylate and neodymium trinaphthenates.

4. A process as claimed in claim 1, characterised in that the organic compounds containing hydroxyl or carboxyl groups are chosen from butyl alcohol and naphthenic acids.

20 5. A process as claimed in claim 1, characterised in that the halogenated compounds are chosen from hydrochloric acid, diethylaluminium chloride, ethylaluminium dichloride, aluminium trichloride, tert.butylchloride, benzyl chloride and benzoyl chloride.

25 6. A process as claimed in claim 1, characterised in that the aluminium organ metal compounds and relative hydride derivatives are chosen from aluminium trialkyl and aluminium alkyl hydrides.

7. A process as claimed in claim 6, characterised in that said aluminium compounds are chosen from triethylaluminium, triisobutylaluminium and diisobutylaluminium monohydride.

8. A process as claimed in claim 1, characterised by adding
5 water to the catalyst in such a quantity that the ratio of the aluminium atoms of the aluminium organometal compound or relative hydride derivative to the added moles of water is between 1:1 and 5:1.

9. A process as claimed in claim 8, characterised in that said
10 ratio is of the order of 2:1.

10. A process as claimed in claim 1, characterised in that the ratio of hydroxyl groups (including those of the water) and/or carboxyl groups to neodymium atoms is of the order of 3:1-30:1, the ratio of neodymium atoms to aluminium atoms is of the order of
15 25:1-80:1, and the ratio of halogen atoms to neodymium atoms is of the order of 1:1-2:1.

11. A process as claimed in claim 1, characterised in that the polymerisation is conducted at a pressure of between 3 and 18 bars absolute.

20 12. A process as claimed in claim 1, characterised in that the polymerisation is conducted between an inlet temperature of the order of 50°-60°C and an outlet temperature of the order of 80°-100°C.

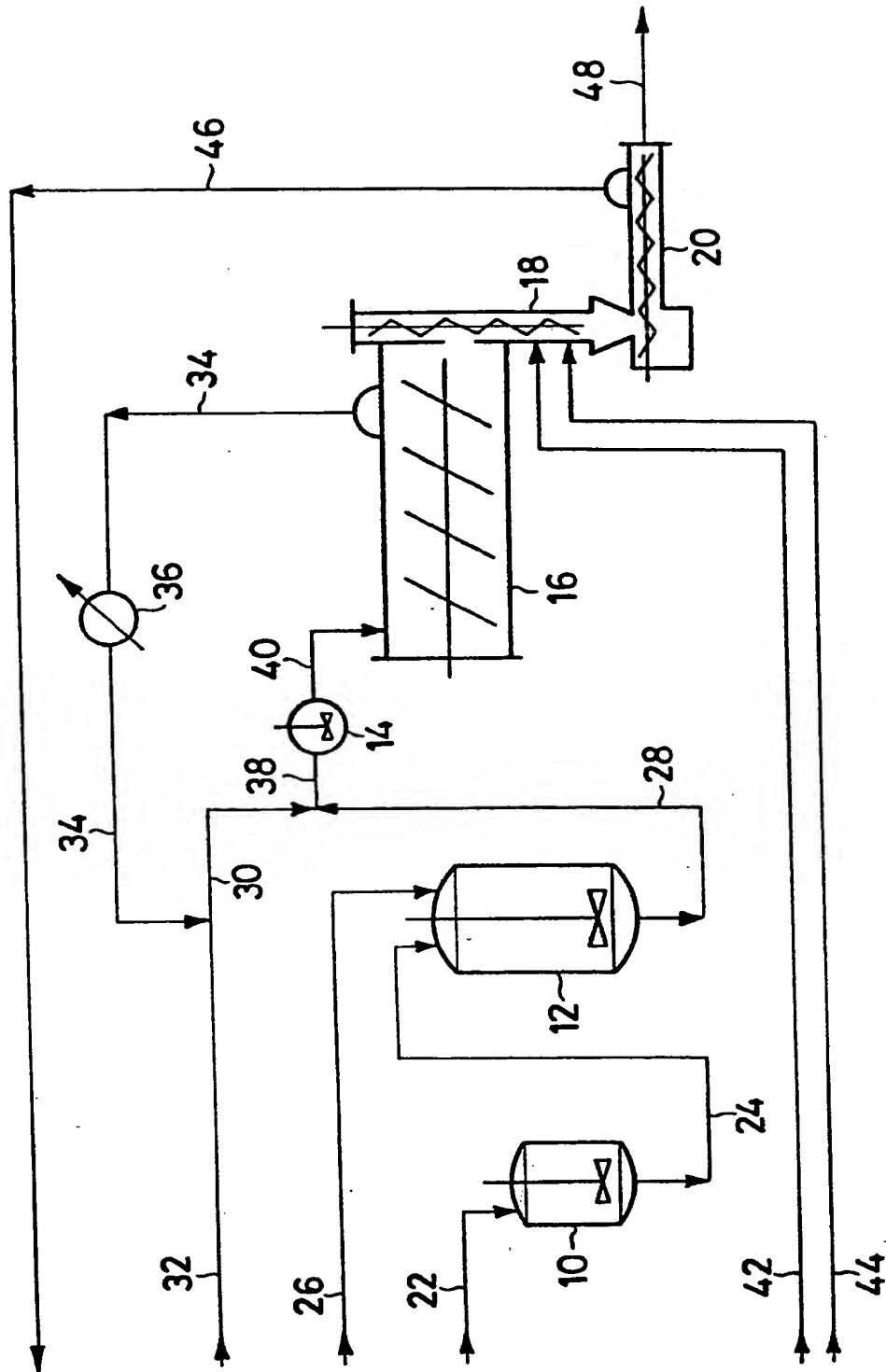
13. A process as claimed in claim 1, characterised in that the
25 residence time during polymerisation varies from 10 to 120 minutes.

14. A process as claimed in claim 13, characterised in that said residence time is of the order of 20-60 minutes.

15. A process as claimed in claim 1, characterised in that the polymerisation is conducted in an apparatus of the self-cleaning single or double extruder type.
16. A process as claimed in claim 1, characterised in that the
5 butadiene monomer evaporated during polymerisation is condensed and recycled directly to the polymerisation stage.
17. A process as claimed in claim 1, characterised in that polymerisation arresting agents and stabilisers against thermo-oxidative degradation are added to the mixture leaving the polymeri-
10 sation stage in a mixing device connected in series with the polymerisation reactor.
18. A process as claimed in claim 17, characterised in that the polymerisation arresting agents are chosen from water and $C_8 - C_{18}$ aliphatic alcohols.
- 15 19. A process as claimed in claim 18, characterised in that basifying compounds chosen from ammonia, amines, epoxides and organic salts (alcoholates and carboxylates, of alkaline metals are added to the water and alcohols.
- 20 20. A process as claimed in claim 17, characterised in that antioxidants and radical capturing agents such as secondary amines and epoxides are associated with the polymerisation arresting agents.
21. A process as claimed in claims 17 to 20, characterised in that said polymerisation arresting agents and said antiradicals are fed in the form of an emulsion in the presence of butadiene.
- 25 22. A process as claimed in claim 1, characterised in that the reaction mixture with its additives is freed of low-boiling substances by operating at a temperature of between 100° and $180^\circ C$

at atmospheric pressure in a heated screw device connected in series with the mixing device of claim 17.

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European Patent
Office

EUROPEAN SEARCH REPORT

0127236

EP 84 20 0716

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
A	FR-A-2 090 960 (BAYER) * Claim 1 *		C 08 F 136/06 C 08 F 2/02 C 08 F 4/52
A	GB-A-2 101 616 (JAPAN SYNTHETIC RUBBER) * Claims 2,7; page 3, lines 20-21 *		
P,A	EP-A-O 092 270 (ENOXY CHIMICA) * Claim 1; page 5, lines 18-19 *		
A	EP-A-O 007 027 (BAYER) * Claim 1 *		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 7)
			C 08 F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 28-08-1984	Examiner VAN HUMBEECK F.W.C.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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